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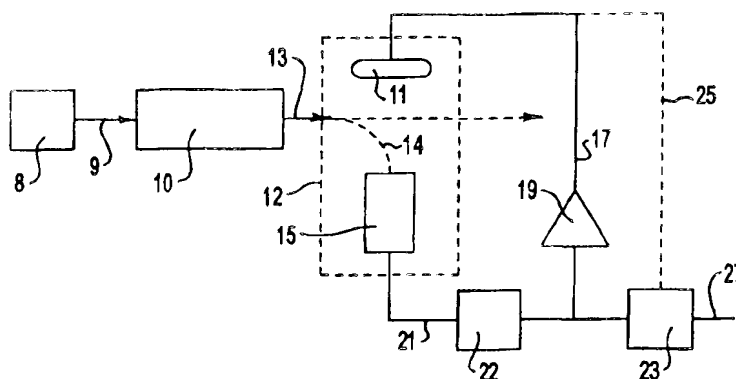


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(71) Applicant (for all designated States except US): VARIAN AUSTRALIA PTY. LTD. [AU/AU]; 679 Springvale Road, Mulgrave, VIC 3170 (AU).			
(72) Inventor; and			
(75) Inventor/Applicant (for US only): GREGORY, Robert, Paul [GB/AU]; 12 Vernon Street, Blackburn South, VIC 3130 (AU).			
(74) Agent: PHILIPS ORMONDE & FITZPATRICK; 367 Collins Street, Melbourne, VIC 3000 (AU).			

(54) Title: DETECTOR SYSTEM FOR MASS SPECTROMETER



(57) Abstract

The invention involves a mass spectrometer that includes a detector system having an electron multiplier detector. Feedback from the output of the detector is used to modify the input ion beam and thereby extend the dynamic measurement range of the spectrometer relative to that of the detector. The mass spectrometer includes means (8) for generating a beam of ions (9) for analysis in mass analyser (10) and then detection by an electron multiplier detector (15). Feedback circuit (17) including conditioning circuit (19) provides a signal to ion lens (11) for dynamically modifying the intensity of the ion beam incident on the detector (15) in dependence upon an output signal (21) from the detector whereby the intensity range of the incident ion beam is limited to within the dynamic range of the detector. Lens (11) deflects ions (14) from beam (13) which emerges from mass analyser (10) into the detector (15). Alternatively, an ion lens may deflect ions away from the detector. The ion beam may also be modified before it enters the mass analyser. The output signal (21) from the detector (15) is oppositely modified, for example by a computer (23), to compensate for the modification to the incident ion beam whereby a corrected output signal (27) representing the intensity of the unmodified ion beam is provided.

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DETECTOR SYSTEM FOR MASS SPECTROMETER

TECHNICAL FIELD

5 This invention relates to a mass analysis spectrometer that includes a detector system having an electron multiplier. The invention is applicable to any mass analysis apparatus involving the generation, mass analysis and detection of a beam of ions, such as for example, an inductively coupled plasma (ICP) mass spectrometer.

10

BACKGROUND

 It is known to use electron multiplier detectors in mass spectrometers in two modes. One mode is a pulse counting operation wherein an electrical charge output pulse is generated for each ion received. This charge pulse is generally sufficiently different from that of noise generated in the electron multiplier itself to enable rejection of a substantial amount of the noise. In addition, the pulse counting mode has a fast response. The dynamic range of an electron multiplier detector operated in the pulse counting mode is limited to, for example, six decades starting from zero ion arrival rate. Above a certain ion arrival rate, the detector will saturate. The other mode of operation for the same detector is an analog mode. Analog mode detectors have their output charge pulses continuously integrated. The primary disadvantages of this method of operation are a slower speed of response and an inability to reject any noise charge pulses originating within the detector. This makes such a method of operation unsuitable for low ion arrival rates. The primary advantage is that the detector may be operated at very high ion arrival rates. The dynamic range is still limited, but the range may be adjusted to cover ion arrival rates well in excess of that capable of being measured by the pulse counting mode.

30

 A mass spectrometer system may have a signal dynamic range in excess of that of an electron multiplier detector in the system. It is known to

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extend the dynamic range of an electron multiplier detection system for ion arrival rates that include zero by using the detector in two modes. The pulse counting mode may be used for low signals and the analog mode for intense signals. Dual output electron multipliers, also known as simultaneous mode
5 electron multipliers, are marketed by ETP Scientific of Auburne, Mass., USA and Galileo Electronics Corp. of Sturbridge, Mass., USA. These detectors may combine both functions simultaneously or disable the pulse counting section in the event of excessive ion arrival rate. This arrangement has the ability to extend the dynamic range of a mass spectrometer by about 3 decades by
10 adding the analog section. Any "dual mode" detector arrangement has some disadvantages. It is expensive and complex since it requires two power supplies, two sets of signal processing electronics plus arrangements to switch between the two modes. It also requires calibration routines, one for each mode plus means to ensure continuity of calibration at the transition between
15 the modes. An example of this known art is the spectrometer system disclosed in United States Patent No. 5463219. Additionally, an electron multiplier exposed to high ion flux will suffer contamination and reduced operating life.

It is also known to use an electrostatic steering lens in conjunction with an electron multiplier detector. An example of this prior art is disclosed in
20 United States Patent No. 5426299. The steering lens provides means to deflect the ion beam either towards or away from the detector depending on a control signal applied to the lens. By virtue of this, the fraction of the ion beam incident on the detector cathode may be controlled. The steering lens control signal is adjusted to cause substantially all the ion beam to impact the detector
25 cathode when measuring low intensity ion fluxes. When measuring high intensity ion fluxes the control is adjusted to ensure that only a small percentage of the ion beam impacts the detector cathode thereby preventing overload of the electron multiplier by excessive ion intensity. A disadvantage of this prior art is that when an unknown sample is presented to the mass
30 spectrometer, one or more scans of each ion signal in the sample that is presented have to be conducted to gain prior knowledge of the signal intensity for each ion. A decision is then made at which sensitivity to measure each

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type of ion within that signal. The sensitivity chosen is one which will avoid detector overload whilst providing adequate sensitivity. Thus, there is a need for multiple scans to effect the final measurement

5 DISCLOSURE OF THE INVENTION

It is an object of this invention to provide a method and apparatus for extending the dynamic range of a detector system within a mass spectrometer which reduce at least some of the above disadvantages.

10 The invention involves a mass spectrometer that includes a detector system having an electron multiplier detector. The invention is applicable to such a system that is operated in the pulse count or analogue mode, including dual mode detectors.

15 In a first broad aspect, the invention provides a mass spectrometer that includes

means for generating a beam of ions for mass analysis,

an electron multiplier detector for the beam of ions, and

20 means for dynamically modifying the intensity of the ion beam incident on the detector in dependence upon an output signal from the detector whereby the intensity range of the incident ion beam is limited to within the dynamic range of the detector, and

means for oppositely modifying the output signal from the detector to compensate for the modification to the incident ion beam whereby a corrected output signal representing the intensity of the unmodified ion beam is provided,

25 whereby the dynamic range of the spectrometer is increased relative to that of the detector.

30 In a second broad aspect, the invention provides a method for expanding the dynamic measurement range of an electron multiplier detector in a mass spectrometer wherein the mass spectrometer includes means for generating a beam of ions for mass analysis and then detection by the detector, the method including

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- (i) dynamically modifying the intensity of the beam of ions incident on the detector in dependence upon an output signal from the detector to limit the intensity range of the incident ion beam to within the dynamic range of the detector, and
- 5 (ii) oppositely modifying an output signal from the detector to compensate for the modification to the incident ion beam to provide a corrected output signal representing the intensity of the unmodified ion beam.

Preferably the electron multiplier detector operates in a pulse-count
10 mode because this provides a measurement range from zero upwards.

In a more particular aspect of the invention, the method and the means for dynamically modifying the ion beam intensity incident on the detector involves the use of one or more ion lenses. The lens (or lenses), which may be electrostatic or magnetic in nature, is (or are) arranged for steering the ions in
15 the ion beam towards or away from the ion sensitive input electrode of the electron multiplier detector to vary the percentage of ions impacting on that electrode.

The invention includes arrangements wherein the ion lens is structurally a part of the detector assembly.

20 Preferably the ion lens(es) is (or are) operated to steer the ions in dependence upon a signal which is fed back from the output of the detector and appropriately conditioned. This allows for the detector output to be monitored continuously and a steering lens control signal adjusted continuously, as a function of the detector output, in such a way as to adjust
25 the proportion of ions that are incident upon the detector's input electrode to keep that proportion below a level that will saturate the detector. That is, when a strong signal is sensed by the electron multiplier detector, this results in a large output and the steering lens control signal is automatically adjusted to reduce the proportion of incident ions that will reach the electron multiplier.
30 This reduces the sensitivity of the detection system and protects the electron multiplier from overload. When a weak signal is sensed by the electron multiplier, the steering lens control signal is automatically adjusted to increase

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the fraction of ions incident on the electron multiplier and maximise the sensitivity without danger of overload. The sensitivity of the detector is thus varied continuously with the intensity of the detected signal at the detector's output by use of output signal feedback.

5 An advantage provided by the above described feedback arrangement for the ion lens is that the sensitivity of the ion detection system is controlled without the need to obtain prior knowledge of the signal intensity for each ion, as in the prior art. The sensitivity of the lens and detector system is automatically and continuously adjusted depending on the strength of the
10 incident ion beam.

Another advantage over detectors that directly measure high ion intensities is that the detector is subjected to reduced contamination effects of the ions themselves, thereby extending the life of the detector.

The method and means for oppositely modifying an output signal from
15 the detector to compensate for the modification to the incident ion beam to provide a corrected output signal may be realised using software or hardware. In a software realisation, a known and progressive relationship or function between the detector output and ion input intensity for controlling the ion lens control signal can be represented graphically, and thus reversed for correcting
20 the output, for example by using a "look up table" technique.

A hardware realisation for oppositely modifying the output signal may include means for providing an inverse function to that of the ion arrival rate from the mass spectrometer vs the rate of ion incidence on the detector as produced by the voltage applied to the ion lens.

25 By arranging a suitable mathematical function for the relation between the sensed output of the electron multiplier detector and the steering control signals for the ion lens, the spectrometer may be calibrated for each ion. Any sample may be presented to the mass spectrometer within the range capable of being controlled by the ion lens and directly measured without previously
30 setting the sensitivity, which is automatically adjusted. Thus the detection system is desensitised with increasing ion signal strength and resensitized for decreasing ion signal strength. The sensitivity is known from the measurement

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itself and the output can be corrected to indicate the true intensity of incident ions before the steering lens.

In comparison to the prior art, the invention enables direct measurement of unknown ion signals without the need for pre-scan readings at reduced
5 sensitivity to look for very intense signals. With some embodiments of the invention, it is possible to adjust the detection system so that a six (6) decade output range from the detector may be representative of nine (9) decades of input ion intensity whilst still retaining a known and progressive relationship between detector output and ion input intensity. This provides a mass
10 spectrometer that has a detector operating in pulse mode which is capable of handling 9 decades of variation in input ion intensities without overloading the detector. A greater than 9 decades range may be provided depending on practical limitations. One such limitation is that at very high attenuations the fraction of the original ion population that is actually measured is very small.
15 With such small fractions, the detected ions may become less representative of the population in the presence of noise and statistical variations. The other limitation is that the deflection lens system geometry and ion energies may prevent very high attenuation of the incident beam.

20 BRIEF DESCRIPTION OF THE DRAWINGS

An embodiment of the invention will now be described, by way of non-limiting example only, with reference to the accompanying drawings.

In the drawings:

25 Figs. 1 to 4 are schematic block diagrams illustrating the functioning of various embodiments of the invention.

Fig. 5 is a graph illustrating the relative sensitivity response of a number of different mass ions incident at a detector as a function of voltage applied to the deflection electrode(s) of an ion lens.

30 Fig. 6 is a graph showing an example relationship between the output range of a detector and the input ion intensity (prior to the ion lens), and

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Fig. 7 is a circuit diagram of an example signal conditioning feedback arrangement.

DETAILED DESCRIPTION OF EMBODIMENTS

5

The invention specifically relates to the detection system of a mass spectrometer. As mass spectrometers are known, a full description thereof will be omitted. The above referenced prior art specifications, namely US 5463219 and US 5426299, both provide a comprehensive description of an ICP mass spectrometer and reference may be had to these specifications for full descriptions of example spectrometers to which this invention is applicable. Thus the description with reference to the figures provided herein refers to only those features of the invention that affect the ion beam that enters or emerges from the mass analyser of the spectrometer.

15 In Figs 1 to 4 the same components have been accorded the same reference numeral. Figure 1 schematically shows a mass analyser 10 and an "off-axis" electron multiplier detector 15 in a mass spectrometer. A beam of ions 9 from means 8 for generating the ions enters the mass analyser 10 for mass analysis and emerges as beam 13. A deflection electrode of an ion lens 20 11 is arranged for steering ions 14 from ion beam 13 that emerges from the mass analyser towards the input cathode of the electron multiplier detector 15. The ion steering lens may be in any position preceding the ion sensitive electrode of an electron multiplier detector system to influence the ability of ions to be detected. The detector input may be the cathode of the electron multiplier 15 or it may be a conversion dynode prior to the electron multiplier 25 cathode. The ion steering lens 11 must precede the electrode of the detector 15 which is used to sense the ions 14, whether this is a conversion dynode or the electron multiplier cathode. The ion steering lens 11 may physically be within the assembly that contains the electron multiplier 15, between the output 30 of the mass analyser 10 and the input of the detector assembly (as represented by the box 12 in dashed outline in Figures 1 and 2).

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A feedback circuit 17 containing a signal conditioning arrangement 19 is connected between the output 21 of the detector 15, following a signal conditioning circuit 22, and the deflection electrode of ion lens 11. A signal conditioning circuit 22 is required between the detector output 21 and the feedback circuit 17 to convert the detector signals to levels which may be measured by the following system. For example, for a detector 15 operating in the pulse counting mode, circuit 22 would comprise a pulse amplifier and level discriminator to distinguish between signal and noise pulses. The discriminator outputs electronic logic level pulses for each pulse from the detector. For a detector operating in the analogue mode, circuit 22 would comprise a high gain current amplifier stage with integration that produces a DC signal in relation to ion arrival rate.

The conditioned feedback or control signal applied to the ion lens electrode 11 varies the percentage of ions 14 that are deflected from beam 13 into the detector 15. Box 23 connected to the output 21 of the detector 15 represents means for oppositely modifying the output signal on line 21 to compensate for the modification to the incident ion beam 13 caused by the feedback control signal applied to electrode 11. There is a functional relationship between this compensation and the feedback signal which is represented by dashed line 25. Reference 27 refers to a corrected output from block 23 which represents or is a measure of the intensity of the unmodified ion beam 13.

Figure 2 schematically shows a similar arrangement to that of Figure 1 except that the detector 15 is arranged on the ion flight axis of the mass spectrometer rather than off it. In this arrangement the ion lens 11 is operative to deflect ions 14 away from the detector 15.

In the arrangement schematically illustrated by figure 3, the ion lens 11 is arranged to steer ions 14 from ion beam 9 into an "off-axis" mass analyser 10. Figure 4 illustrates a further alternative wherein the ion lens 11 deflects ions 14 away from the ion beam 9 that enters the detector 15. Thus, the arrangements of Figures 3 and 4 show a positioning of the ion lens 11 in front of the mass analyser.

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As will be evident from figures 1 to 4, the invention includes arrangements wherein an ion steering lens is provided as a separate component to a detector, in which case the lens could be located before or after the mass analyser, and arrangements wherein an ion lens and detector
5 are provided as the one structural component (as represented by dashed box 12 in Figs 1 and 2), in which case the assembly may include one or more lenses, a conversion dynode and electron multiplier.

The schematically illustrated ion lens electrode 11 may be part of an electrostatic steering lens or a magnetic steering lens. An electrostatic steering
10 lens influences the ion trajectories by virtue of the electrode 11 potential generating an electrostatic field which interacts with the electrostatic charge carried by the ions to thus steer the ions. A magnetic steering lens steers the ions by the interaction of the magnetic field with the electrostatic charge carried by the ions.

15 The Fig. 5 graph describes the relative sensitivity response of a number of different mass ions (i.e., ${}^6\text{Li}^+$, ${}^{115}\text{In}^+$ and ${}^{232}\text{Th}^+$, as labelled on the graph) incident at a detector 15 as a function of voltage applied to the deflector electrode 11 of an ion lens. This response is substantially exponential with the deflector volts. By using signal negative feedback to derive the deflector
20 voltage, this exponential response will produce a logarithmic relationship between ion arrival rate from the mass spectrometer and the rate of ion incidence upon the electron multiplier detector.

Fig 6 illustrates graphically a progressive relationship between the output 21 of an electron multiplier detector 15 that has about a 6 decade range
25 and about a 9 decade range of ion intensity in a beam 13 emerging from a mass analyser 10. The conditioning of the feedback signal by signal conditioning means 19 is determined according to this relationship. It also determines the correction factor for any measurement that must be applied to the output signal.

30 In Fig 6, the ordinate shows the output range from a detector 15 and the abscissa the input ion intensity in a beam 13 prior to a steering lens electrode 11. Nine (9) decades of ion measurement is achieved with $6.5 \cdot 10^6$

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output from the detector. This is a dynamic range extension of 150. The graph shows two distinct regions of response. There is a region at lower ion arrival rates where the relation to measured output is substantially linear. This is desirable since at low ion arrival rates the relative noise in the data is larger and may compromise any nonlinear signal conditioning, for example by adding a bias to signal estimates. Ion signal measurement is subjected to a natural phenomenon known as "shot noise", which is known to decrease in relative significance as the signal measured at the detector increases. By confining the data compression to a region of higher ion arrival rates, seen as a second, logarithmic, region in figure 3, the relative effects of shot noise are diminished. The performance with and without signal feedback would be indistinguishable for low ion arrival rates, but feedback will enable the same detector to measure effective ion signals beyond the normal capability of the detector.

Figure 6 may be generally described by observing that the deflector lens response in figure 5 exhibits an exponential relationship between signal intensity and lens voltage. If this were not the case, then a suitable mathematical function could be added in the feedback loop 17 to produce this effect. By virtue of signal feedback, the relation between effective input ion rate and measured output rate may then be described by the following equation:

$$V_o = V_i \exp(-a V_o)$$

where V_o is the measured output signal, V_i the effective input signal and 'a' is a constant derived from the gain in the feedback loop. By taking the logarithms of both sides, the relationship is described as:

$$\log(V_o) = \log(V_i) - a V_o$$

It is seen that when aV_o is small compared with $\log(V_o)$, the relationship is substantially linear:

$$\log(V_o) = \log(V_i) \quad aV_o \ll \log(V_o)$$

This is true for small V_o or low measured ion rate and describes the lower linear region of figure 6. Similarly, when aV_o is large compared with $\log(V_o)$ then the relationship is substantially logarithmic:

$$aV_o = \log(V_i) \quad aV_o \gg \log(V_o)$$

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This is the case for large measured ion rate and describes the upper logarithmic region in figure 6. The transition between the two response regions in figure 6 may be adjusted by the gain, 'a', used in the feedback loop.

If the response to deflector volts on the steering lens 11 is not as
5 desired, the mathematical relation between the detector 15 output signal 21 and the deflector lens voltage may be manipulated either by hardware or software in the feedback path 17 to derive a response such as in figure 6. For instance, if the ion response to deflector volts is only linear and a logarithmic sensitivity function such as in figure 6 is desired, then an antilogarithmic
10 function may be used in the feedback path. A logarithmic function is only one example of numerous mathematical response functions that could be employed by the invention for the dynamic range extension.

Similarly, to correct the measured data to reflect actual ion arrival rate from the mass spectrometer, it is necessary to reference the data from figure 6.
15 This may be done in software by storing the calibration curves for a number of ions or by the use of a hardware circuit of inverse function to that of the modifying system. Thus block 23 may be a programmed computer or an output circuit which receives a lens control signal on line 25.

Fig. 7 shows a detector feedback control circuit, that is, a signal
20 conditioning arrangement as represented by 19 in fig. 1. This circuit is suitable for monitoring the pulse outputs from a detector 15 which is operated in the pulse counting mode. The detector output pulse rate is periodically sampled from the output of circuit 22 and derives a varying DC deflector output voltage on line 17 in response to this pulse rate.

25 In the Fig. 7 circuit, pulse rate sampling on line 30 is by means of a data counter using integrated circuits 35, 36 and 37. Count data is latched at the end of a count interval using IC's 38 and 39. This latched data is used to drive a digital to analogue converter, 40, 41 and 43. IC32 is a counter/divider which derives the data sampling interval whilst 33 is a decade counter whose outputs
30 operate at the end of a count period sequentially enabling the data latch, resetting the data counter and together with 32, enabling the data counter for another period. IC44 is to prevent data "wrap around" when the input data rate

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exceeds the capability of the counter circuit. IC42 scales the count response and the offset adjustment 45 is provided to tune the deflector or steering lens response on line 46, which may also be achieved remotely via an external deflection control input 47. Switch 48 is provided to disable the feedback
5 control action. This switch 48 may be operated remotely and feedback may be disabled for conventional pulse counting mode operation or for lens response calibration purposes.

A circuit for performing the same functions as the Fig. 7 circuit could be provided otherwise than by using the discrete integrated circuits of that Fig., for
10 example by using a programmable logic integrated circuit. Also the resolution of the digital to analogue converter may be varied along with the size of the data counter and sample interval to cope with different sampling periods or different ranges of ion pulse rates.

Other embodiments of the invention include:

- 15 a) operating an electron multiplier detector in the pulse counting mode, measuring output current and converting this to a voltage which is applied to the deflection electrode(s) of an ion lens(es).
- b) operating an electron multiplier detector in the analogue mode, measuring output current and converting this to a voltage which is applied to
20 the deflector electrode(s) of an ion lens(es)

Variations, modifications and/or additions other than those specifically described can be made to the invention and it is to be understood the invention includes all such variations, modifications and/or additions which fall within the
25 scope of the following claims.

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CLAIMS:

1. A mass spectrometer including,
means for generating a beam of ions for mass analysis,
5 an electron multiplier detector for the beam of ions, and
means for dynamically modifying the intensity of the ion beam incident
on the detector in dependence upon an output signal from the detector
whereby the intensity range of the incident ion beam is limited to within the
dynamic range of the detector, and
10 means for oppositely modifying the output signal from the detector to
compensate for the modification to the incident ion beam whereby a corrected
output signal representing the intensity of the unmodified ion beam is provided,
whereby the dynamic range of the spectrometer is increased relative to that of
the detector.
- 15 2. A mass spectrometer as claimed in claim 1 wherein the means
for dynamically modifying the intensity of the ion beam incident on the detector
includes at least one ion lens.
3. A mass spectrometer as claimed in claim 2 including a mass
analyser through which the ion beam passes before detection by the electron
20 multiplier detector, wherein the ion lens is located for modifying the ion beam
between the mass analyser and the detector.
4. A mass spectrometer as claimed in claim 3 wherein the ion lens
is operative to modify the intensity of the ion beam incident on the detector by
steering ions from the ion beam into the detector.
- 25 5. A mass spectrometer as claimed in claim 3 wherein the ion lens
is operative to modify the intensity of the ion beam incident on the detector by
deflecting ions from the ion beam away from the detector.
6. A mass spectrometer as claimed in claim 2 including a mass
analyser through which the ion beam passes before detection by the electron
30 multiplier detector, wherein the ion lens is located for modifying the ion beam
prior to its passage through the mass analyser.

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7. A mass spectrometer as claimed in claim 6 wherein the ion lens is operative to modify the intensity of the ion beam incident on the detector by steering ions from the ion beam into the mass analyser.

8. A mass spectrometer as claimed in claim 6 wherein the ion lens
5 is operative to modify the intensity of the ion beam incident on the detector by deflecting ions from the ion beam away from the mass analyser.

9. A mass spectrometer as claimed in any one of claims 2 to 8 including a feedback circuit connected between the output of the detector and the ion lens for providing a control signal for the ion lens, wherein the feedback
10 circuit includes signal conditioning means for modifying a feedback signal to produce the control signal according to a predetermined function between the detector output and the unmodified ion beam intensity.

10. A mass spectrometer as claimed in claim 9 wherein the means for oppositely modifying the output signal from the detector to compensate for
15 the modification to the incident ion beam includes a programmable computer connected to the detector output which is programmed to reverse the modification applied to the feedback signal according to the predetermined function, whereby the computer provides an output which represents the unmodified ion beam intensity.

20 11. A mass spectrometer as claimed in claim 9 wherein the means for oppositely modifying the output signal from the detector to compensate for the modification to the incident ion beam includes an output circuit connected to the detector output, wherein the signal conditioning means is connected to said output circuit, wherein the output circuit is operable to reverse the
25 modification applied to the feedback signal according to a signal received from the signal conditioning means, whereby the output circuit provides an output signal which represents the unmodified ion beam intensity.

12. A mass spectrometer as claimed in any one of claims 9 to 11 wherein the predetermined function is linear for low intensities of the incident
30 ion beam and logarithmic for high intensities of the incident ion beam

13. A mass spectrometer as claimed in any one of claims 2 to 12 wherein the ion lens is an electrostatic steering lens.

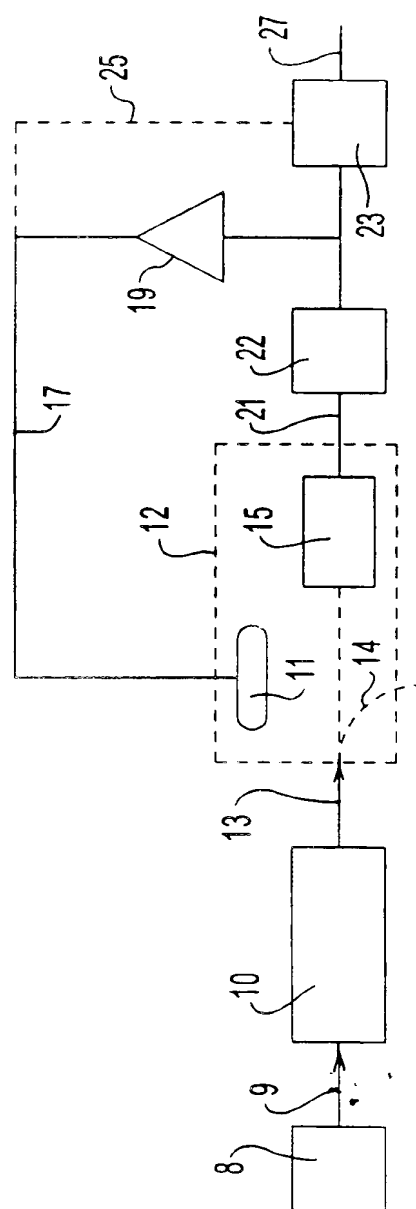
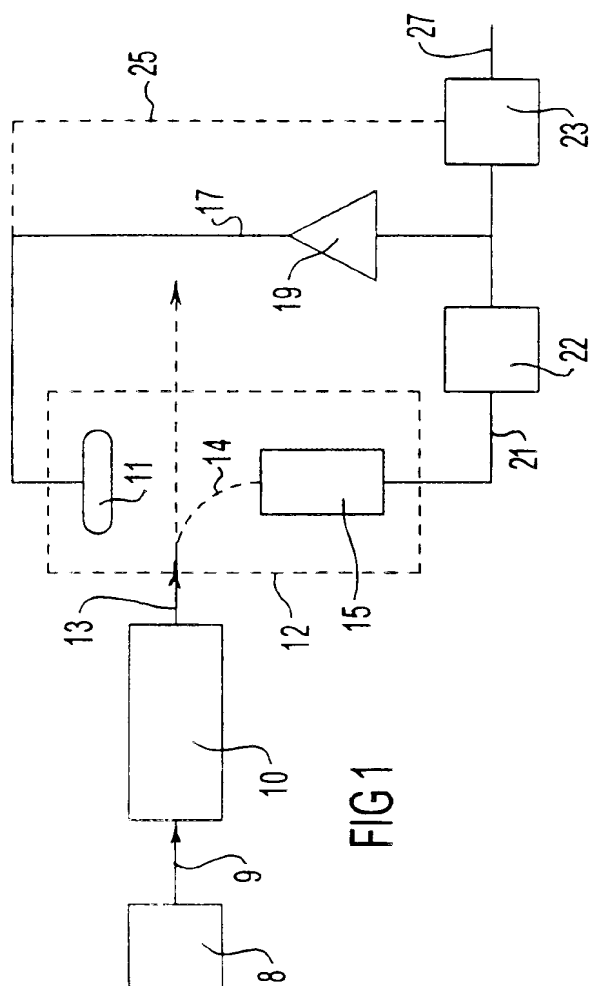
- 15 -

14. A mass spectrometer as claimed in any one of claims 2 to 12 wherein the ion lens is a magnetic steering lens.

15. A mass spectrometer as claimed in claim 2 wherein the ion lens is structurally a part of the detector assembly.

5 16. A method for expanding the dynamic measurement range of an electron multiplier detector in a mass spectrometer, wherein the mass spectrometer includes means for generating a beam of ions for mass analysis and then detection by the detector, the method including

- 10 (i) dynamically modifying the ion beam intensity incident on the detector in dependence upon an output signal from the detector to limit the intensity range of the incident ion beam to within the dynamic range of the detector, and
- 15 (ii) oppositely modifying an output signal from the detector to compensate for the modification to the incident ion beam to provide a corrected output signal representing the intensity of the unmodified ion beam.



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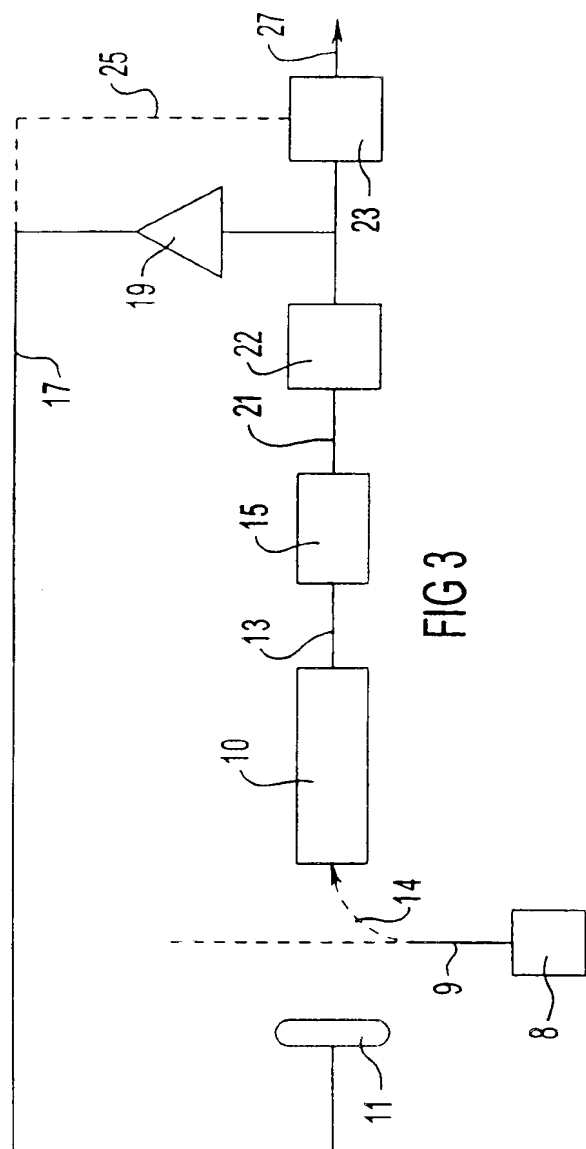


FIG 3

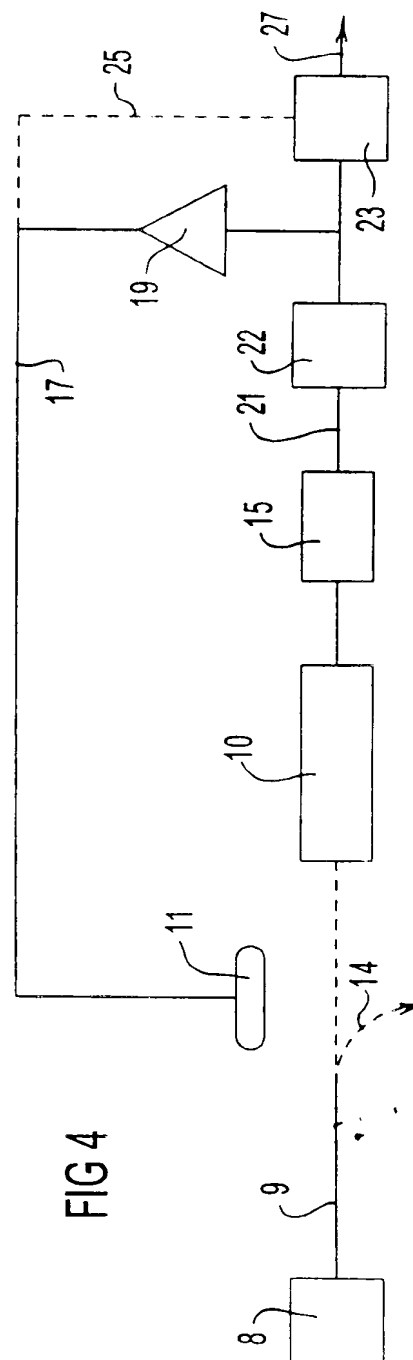
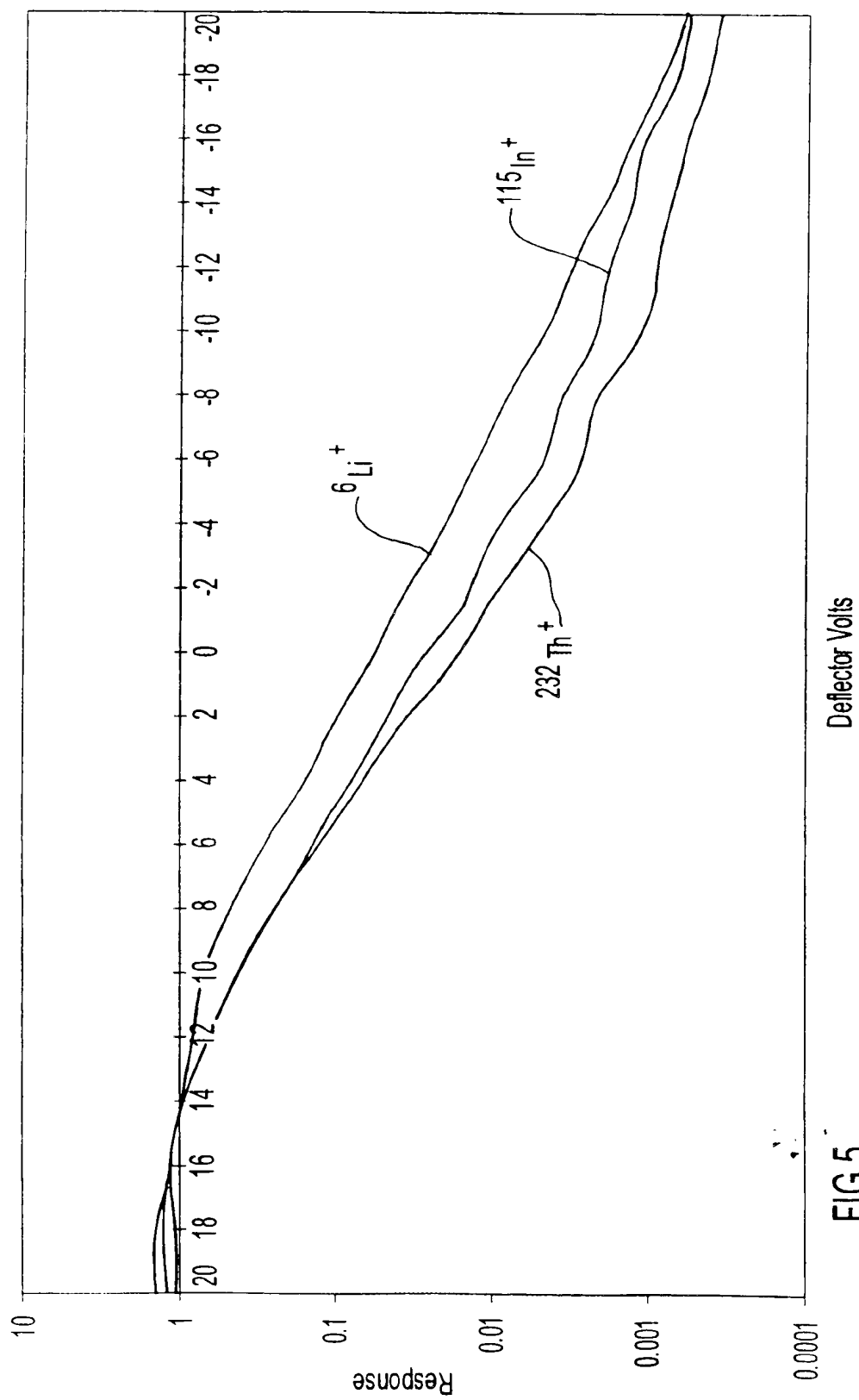


FIG 4

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Deflector Volts

FIG 5

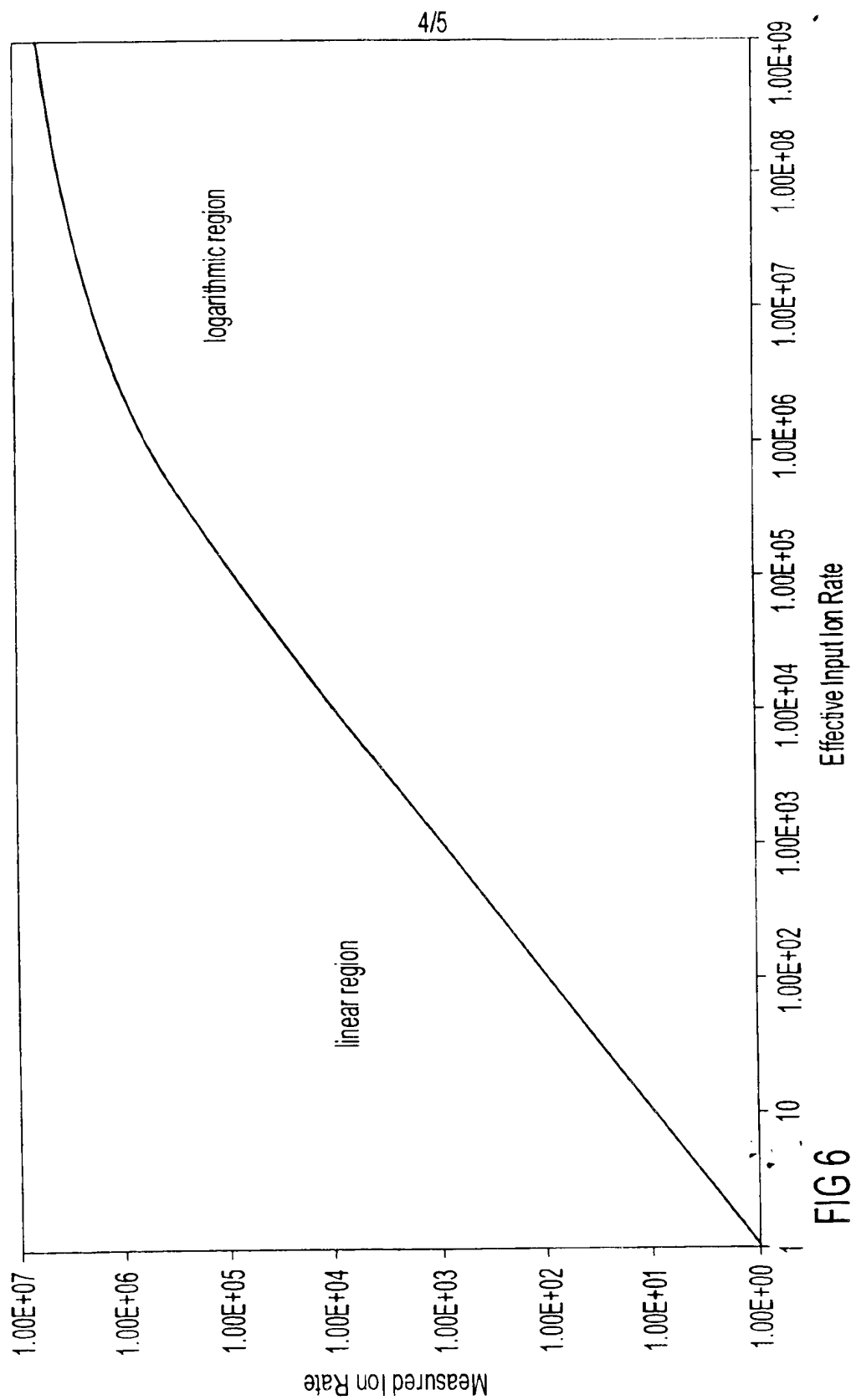
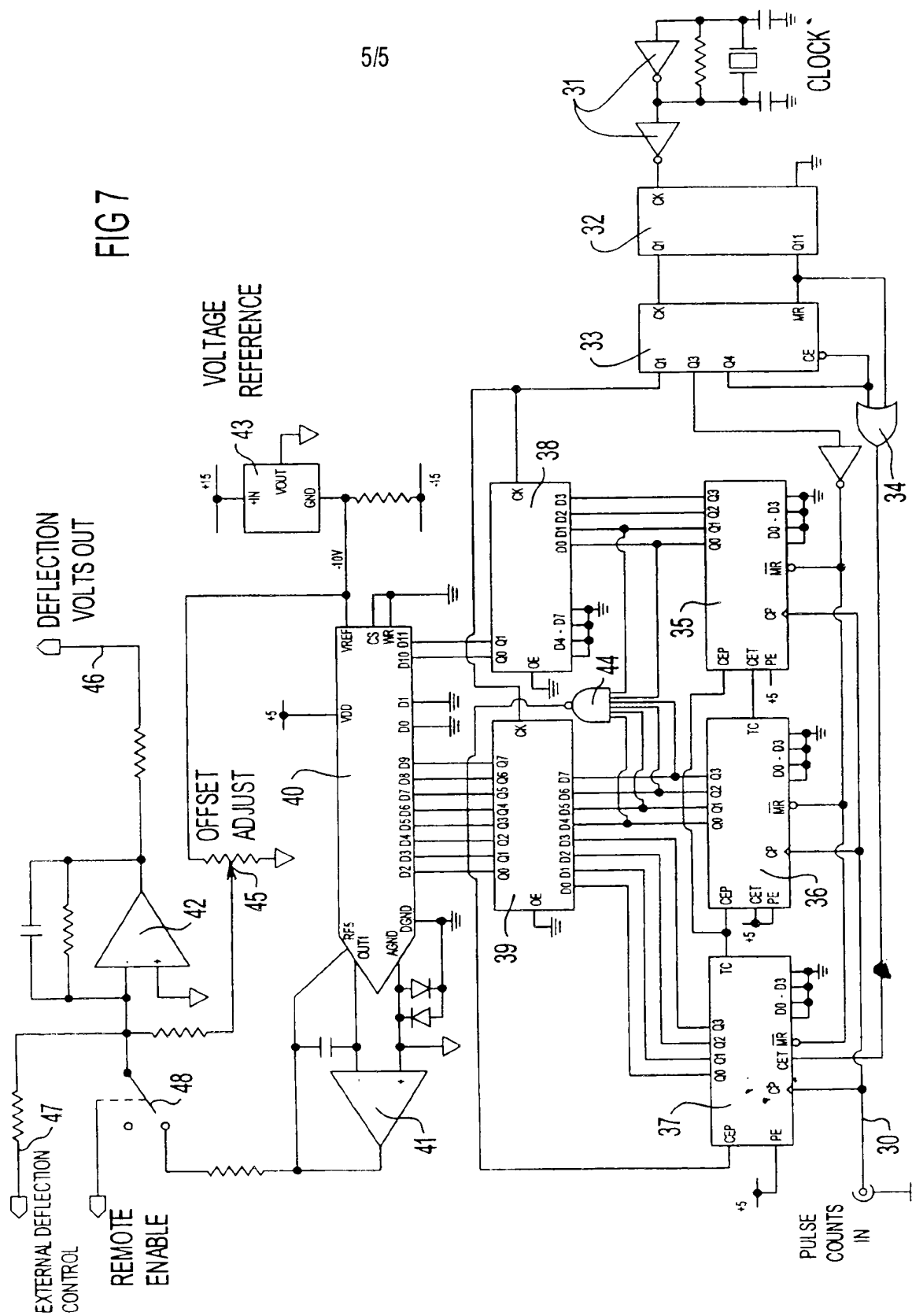


FIG 7



INTERNATIONAL SEARCH REPORT

International Application No.
PCT/AU 98/00319

A. CLASSIFICATION OF SUBJECT MATTER																						
Int Cl ⁶ : H01J 49/02, 49/04																						
According to International Patent Classification (IPC) or to both national classification and IPC																						
B. FIELDS SEARCHED																						
Minimum documentation searched (classification system followed by classification symbols) IPC : H01J 49/02, 49/04																						
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU : IPC as above																						
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPAT, JPAT, USPM : MASS, SPECTROMET., PARTICLE, ION., DETECT., FEEDBACK, ELECTRON, SIMULTANEOUS, MODE, DUAL, PULSE., GAIN#, COUNT:																						
C. DOCUMENTS CONSIDERED TO BE RELEVANT																						
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																				
X	US 5115667 A (BARET) 18 September 1994 Column 1, line 45 - column 2, line 5	1, 16																				
X	Patent Abstracts of Japan, E-1389, page 14, JP5-47346 A (JEOL LTD) 26 February 1993 Abstract	1, 16																				
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex																						
<p>* Special categories of cited documents:</p> <table border="0"> <tr> <td>"A"</td> <td>document defining the general state of the art which is not considered to be of particular relevance</td> <td>"T"</td> <td>later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>"E"</td> <td>earlier document but published on or after the international filing date</td> <td>"X"</td> <td>document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"L"</td> <td>document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"Y"</td> <td>document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>"O"</td> <td>document referring to an oral disclosure, use, exhibition or other means</td> <td>"&"</td> <td>document member of the same patent family</td> </tr> <tr> <td>"P"</td> <td>document published prior to the international filing date but later than the priority date claimed</td> <td></td> <td></td> </tr> </table>			"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	"E"	earlier document but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family	"P"	document published prior to the international filing date but later than the priority date claimed		
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"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art																			
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family																			
"P"	document published prior to the international filing date but later than the priority date claimed																					
Date of the actual completion of the international search 5 June 1998		Date of mailing of the international search report 17 JUN 1998																				
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (02) 6285 3929		Authorized officer RAJEEV DESHMUKH Telephone No.: (02) 6283 2145																				

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU 98/00319

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Patent Abstracts of Japan, E-14, page 55, JP55-46421 (HITACHI SEISAKUSHO K K.) 1 April 1980 Abstract; drawing	1-16
A	Patent Abstracts of Japan, JP 6-109702 A (YOKOGAWA ELECTRIC CORP) 22 April 1994 Abstract; drawing	
A	Patent Abstracts of Japan, JP 6-44944 A (SHIMADZU CORP) 18 February 1994 Abstract; drawing	
A	US 5426299 A (NAKAGAWA et al) 20 June 1995 Column 4, lines 54-65	
A	US 5572022 A (SCHWARTZ et al) 5 November 1996 Column 9, lines 49-61	
A	US 5712480 A (MASON) 27 January 1988 Column 6, lines 13-17	
A	US 4472630 A (SCHOEN) 18 September 1984 Column 5, lines 12-24	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.
PCT/AU 98/00319

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US	5115667	EP	402827	FR	2648616	JP	3064843
US	5426299	JP	6267497				
US	5712480	EP	774773	JP	9147791		
END OF ANNEX							